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Isotope-Exchange Reactions as a Function of Temperature: Isotopic Fractionation in Interstellar Molecules

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A model is used to predict rate constants for primary deuteration reactions which fractionate deuterium in interstellar molecules.

For the molecular species found in dense, interstellar clouds, such as TMC-1 and Orion, the D/H relative abundances range from 0.002 to 0.05, compared to the cosmic D/H ratio of $\sim 2 \times 10^{-5}$ (1). Chemical models for the synthesis of these molecular species must also be able to predict isotopic fractionation. This latter requires rate constants for the isotope-exchange reactions which effect the isotopic fractionation. These rate constants are needed for the temperature range 10 - 100 K but few data are currently available. Modellers are forced to extrapolate from data measured in the range 80 - 300 K or otherwise to guess.

We are interested in predicting rate constants for isotope-exchange reactions as a function of temperature. For the representative isotope-exchange reaction



the rate constant k_f for the forward or exergonic direction [$\Delta G^\circ < 0$], is related by thermodynamics to that for the back reaction k_b , by $k_b = k_f \exp (\Delta G^\circ/RT)$. It has been standard to estimate k_f and k_b as follows (1,2),

$$k_f = k_c \quad (2)$$

$$k_b = k_c \exp (\Delta E/RT) \quad (3)$$

where k_c is the collisional rate constant (3). Our own approach is to model the temperature dependence of k_f and to relate k_b to k_f by thermodynamics. Our analysis replaces (2) by (4) and (3) by (5) as follows

$$k_f = k_c K / (K + 1) \quad (4)$$

$$k_b = k_c / (K + 1) \quad (5)$$

where K is the equilibrium constant for the reaction (1) written in the exergonic direction. Rate constants k may therefore be estimated as a function of temperature from thermodynamic estimates of equilibrium constants K as a function of temperature. We have used this approach for isotope-exchange reactions (4,5): Mautner has independently used the same approach for particle-transfer reactions (6). And the same result

$$k_f + k_b = k_c \quad (6)$$

had been identified prior to this - as an empirical relation from the analysis of experimental data (7-10).

Our previous study (5) examined several representative isotope-exchange reactions for which experimental rate data were available throughout the temperature range 80-300 K; and we showed how these data were well simulated by the model's theoretical predictions (4) and (5). We now use the model to analyze some isotope-exchange reactions which may fractionate deuterium in interstellar

molecules. For some reactions, e.g. (7) and (8), the model seems to work but in others, (9) and (10), it does not. In the latter cases, it is important to be able to understand why.

For the comparison, we have selected primary deuteration reactions listed in Table 1 of Millar et al.'s model of deuterium fractionation in dense interstellar clouds (1). The scheme is as follows. The initial cosmic deuterium reservoir, consisting of deuterium atoms, is ionized by cosmic rays and reacts to form HD by reaction (7). Experimental measurements are restricted to the temperature range 200-300 K (8) and in this range the model predicts the data well (Table 1). At interstellar temperatures, the forward rate constant is effectively at the collision limit and the backward effectively zero. The model provides a reliable way of estimating the magnitude of these, in the absence of experimental data.

TABLE 1. Experimental rate constants (10^{-9} cm³/molec s) predicted by the model

#	REACTION	$-\Delta H^\circ/R(K)$	TEMP.	k_f		k_r	
				EXPT.	MODEL	EXPT.	MODEL
(7)	$D^+ + H_2 = HD + H^+$	462	205	2.2	2.0	0.11	0.14
			295	1.7	1.9	0.17	0.26
			80	1.3	1.5	0.29	0.26
(8)	$H_3^+ + HD = H_2D^+ + H_2$	227	200	1.2	1.2	0.51	0.50
			295	1.1	1.2	0.56	0.58

The primary deutrating molecular species is HD, as formed by reaction (7). It reacts principally by reaction (8) to form H_2D^+ which, in turn, is a facile proton/deuteron donor - able to deuterate a range of interstellar molecules. Table 1 compares, for reaction (8), data down to 80 K (9) with model predictions, which rely on equilibrium constants determined by Herbst (11). These agree, as well for reaction (8) as for (7); and the same conclusions apply to both reactions.

After H_2D^+ , the next most important deutrating species is DCO^+ - especially at low temperatures and early in the development of the galaxy (1). How is DCO^+ itself synthesized (12,13)? One route involves exchange of HCO^+ with the major deuterium reservoirs D and HD: a second is deuteron transfer from H_2D^+ to CO.

TABLE 2. Experimental rate constants (10^{-9} cm³/molec s) not predicted by the model

#	REACTION	$-\Delta H^\circ/R(K)$	TEMP.	k_f		k_r	
				EXPT.	MODEL	EXPT.	MODEL
(9)	$HCO^+ + D = DCO^+ + H$	796	120	0.2	1.4	<0.005	0.0055
			300	0.045	1.2	~0.01	0.26
			460	-	1.0	0.015	0.54
(10)	$HCO^+ + D_2 = DCO^+ + HD$	301	80	<0.0005	1.1	<0.0005	0.02

Both routes to DCO^+ are summarized in Table 2, which again compares experimental data with predictions of the model. For the first route, involving the isotope-exchange reactions (9) and (10), the data are taken from refs. (14,15) and (9,16) respectively. The model uses equilibrium constants estimated as $K_9 = 0.46 \exp(796/T)$ and $K_{10} = 1.13 \exp(301/T)$ (17). Both reactions (9) and (10) show no agreement between experiment and theory. Reaction (10) (and others similar) are prevented by energy barriers which we have identified in the attractive reaction hypersurface (13). Reaction (9) is not "well behaved", in that it shows an anomalous negative temperature dependence; and thus the failure of our model is not surprising. Why is reaction (9) anomalous? We guess that it may derive from the need to conserve angular momentum, the moment of inertia of the products being half that of the reactants.

For the second route, our model predicts that $\text{H}_2\text{D}^+ + \text{CO}$ yields a product ratio $\text{HCO}^+/\text{DCO}^+ = 3.8$ under all conditions. The reaction is equivalent to running the isotope-exchange reaction $\text{DCO}^+ + \text{H}_2 = \text{HCO}^+ + \text{HD}$ at a temperature of $\sim 20,000$ K, because the reaction $\text{H}_3^+ + \text{CO} = \text{HCO}^+ + \text{H}_2$ is exothermic by 1.7 eV (13)! [Thus for $\text{DCO}^+ + \text{H}_2 = \text{HCO}^+ + \text{HD}$, $K = 3.78 \exp(-380/T)$ (17).] The same argument applied to the reaction $\text{CH}_2\text{D}^+ + \text{O} = \text{DCO}^+ + \text{H}_2$ ($\text{HCO}^+ + \text{HD}$), gives the same product ratio $\text{HCO}^+/\text{DCO}^+ = 3.8$ under all conditions.

In conclusion, we have discussed isotope-exchange reactions where the rate constants can be predicted accurately and others where the agreement is poor. Where the model fails, we can often identify this in advance and understand why. Is the model useful for modelling isotopic fractionation in interstellar molecules? For the reactions listed in Table 1, the answer is no. The difference between the rate constants used by the modellers from (2) and (3), and our values from (4) and (5) is negligible compared with the many uncertainties in the astrophysical models (1). On the other hand, the differences can be much larger for the reactions in Table 2. Thus if our guess about reaction (9) is correct, the same behavior may well apply to $\text{H}_3^+ + \text{D} = \text{H}_2\text{D}^+ + \text{H}$, a reaction which is probably important (12). In that case the estimated rate constant may be much too large (1). Finally we suggest that our model will be useful for estimating rate constants for fractionating heavier isotopes such as ^{13}C , ^{15}N , ^{18}O etc. It will be hard to measure these for polyatomic reactants at interstellar temperatures.

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